Oxidation and Aging in U and Pu Probed by Spin-Orbit Sum Rule Analysis: Indications for Covalent Metal-Oxide Bonds

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Introduction

Actinide physics and chemistry are of great interest due to the unique behavior of the 5*f* states that dominate the electronic structure.

How these states evolve with changes in crystal structure, alloying, oxidation state, and radiation damage is of considerable importance to better understand these materials.

Oxidations state: How are the *f* electrons bonding in actinide oxides?

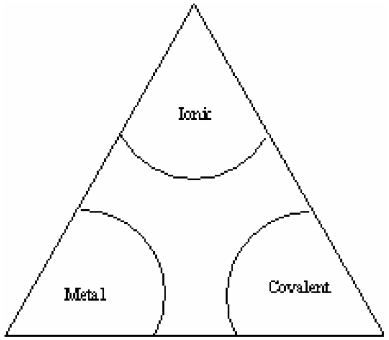
Radiation damage: U and Pu evolve with time due to self-induced radiation damage of the lattice. How does this affect the *f* states?

Our goal here is to examine how **oxidation** and **radiation damage** influence the bonding behavior of the 5*f* electrons in U and Pu.

Why is this important?

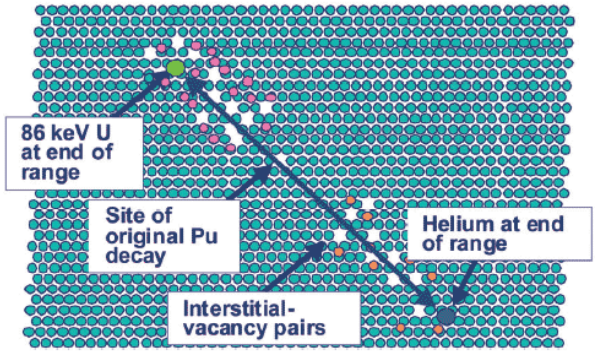
Oxidation:

- ↳ Reactor fuels are composed of actinide oxides.
- ↳ Helps us understand the surface of actinide metals.
- ↳ Understanding what type of bonding is occurring.



Radiation damage:

- ↳ Self-induced radiation damages the lattice of U and Pu.
- ↳ How the *f* states change due to this damage affects the bulk behavior of the metal.



How do we investigate the *f* states?

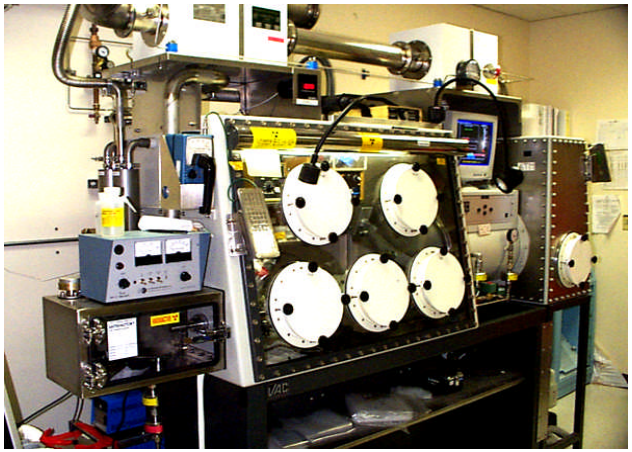
A powerful tool for interrogating the 5*f* states is the spin-orbit sum rule.

↳ Works particularly well for the actinides.

↳ Probes the 5*f* spin-orbit interaction per hole.

In order to use the spin-orbit sum rule, the branching ratio must first be extracted from the spin-orbit split white-lines of absorption spectra.

We record the branching ratio by **electron energy-loss spectroscopy** (EELS) in a **transmission electron microscope** (TEM).

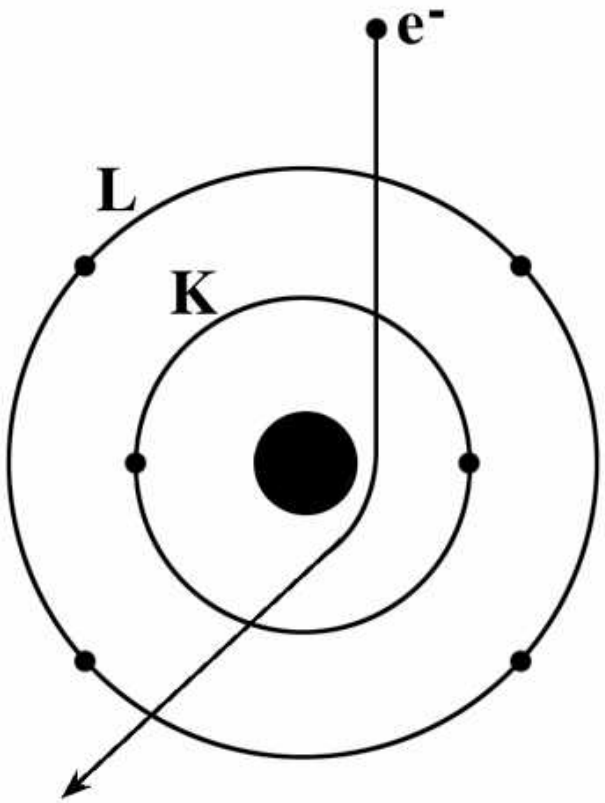


In-house sample prep

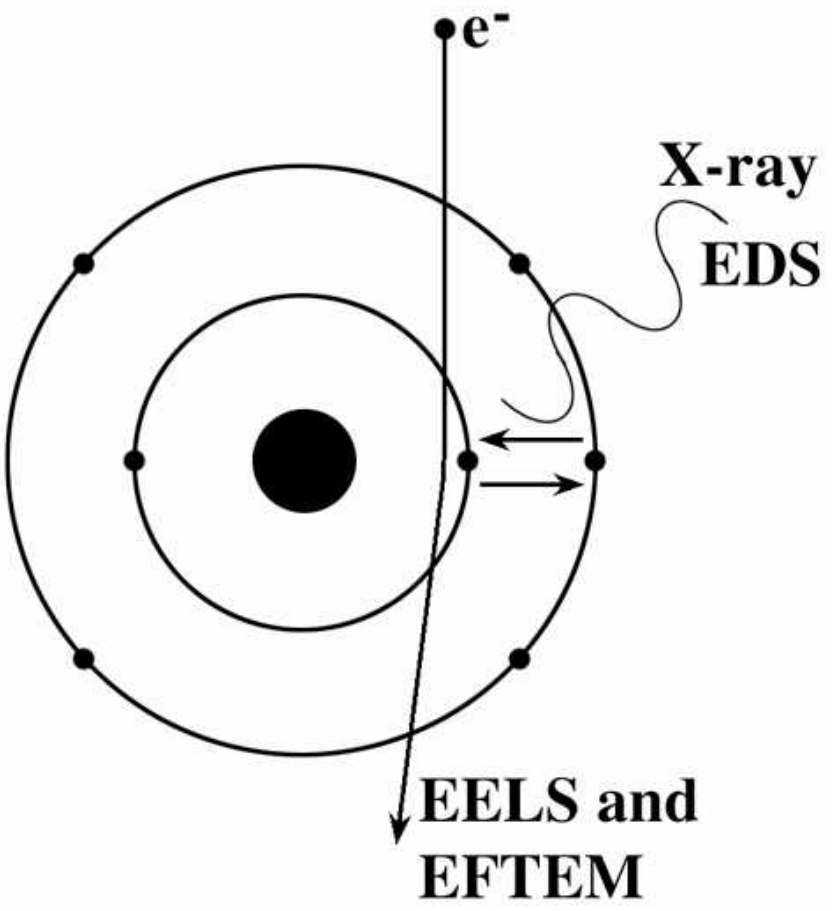
and TEM analysis

Electron Scattering

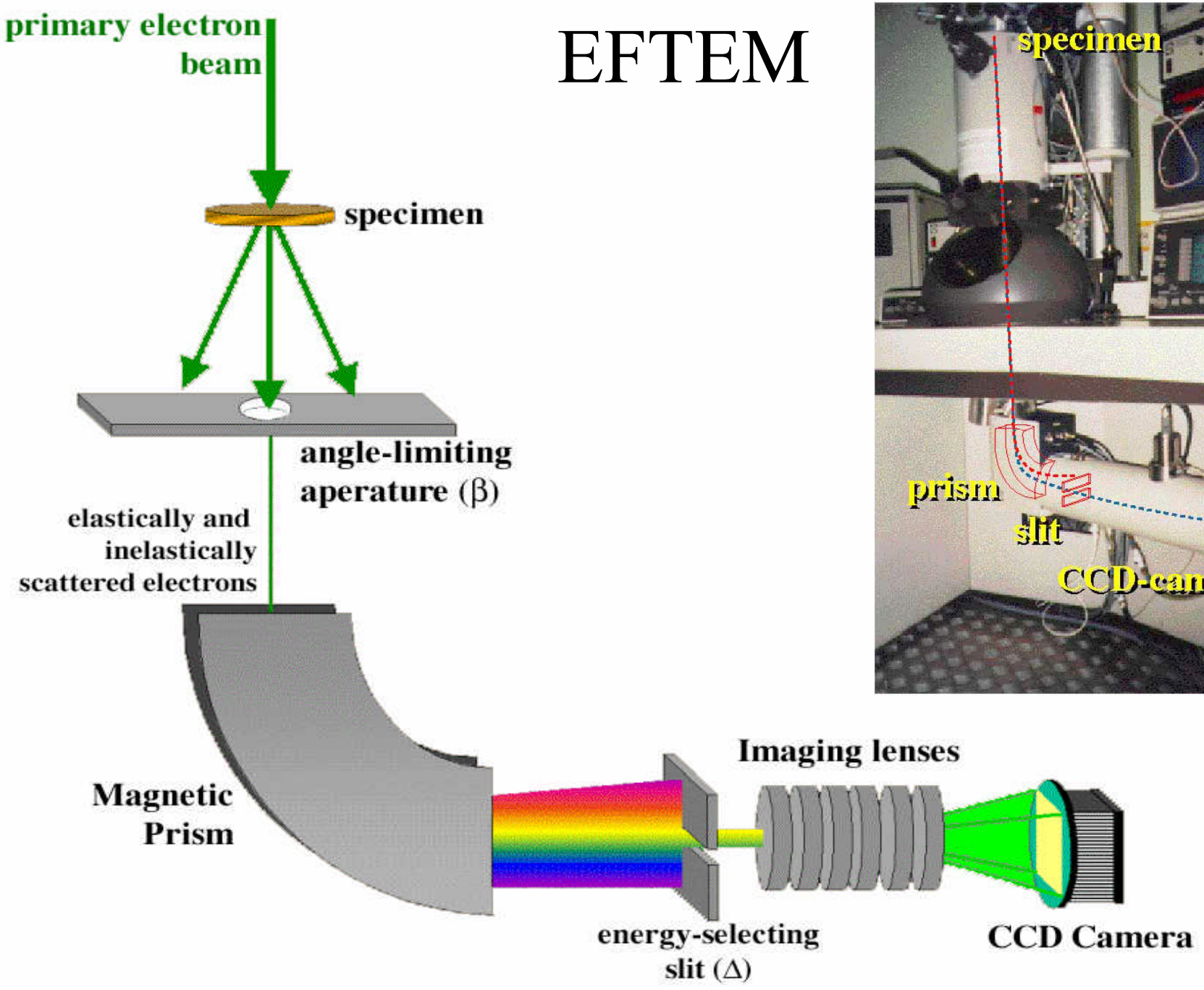
Elastic → Structure

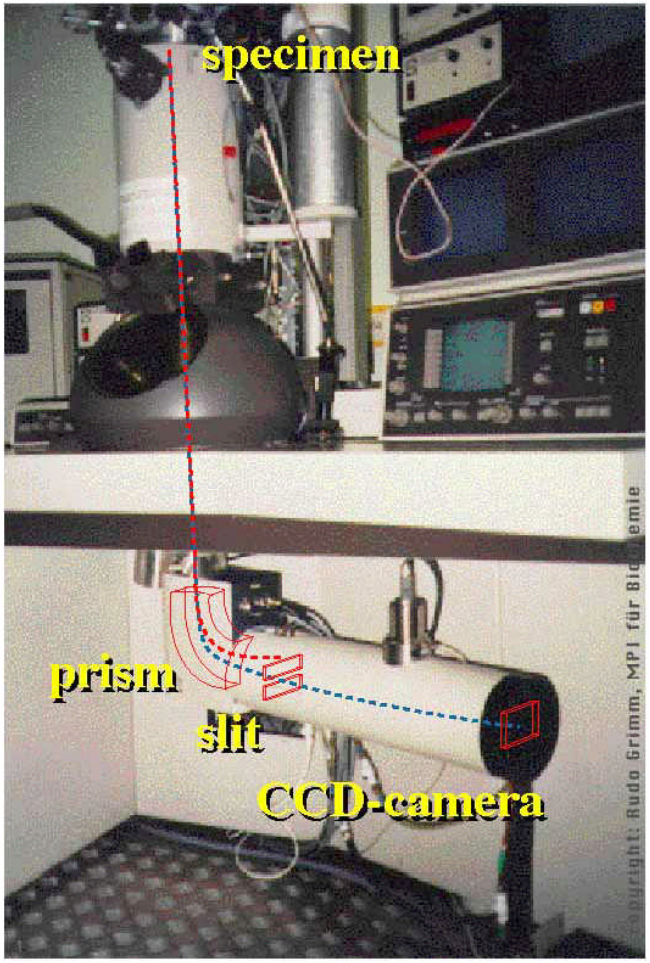


Inelastic → Chemistry

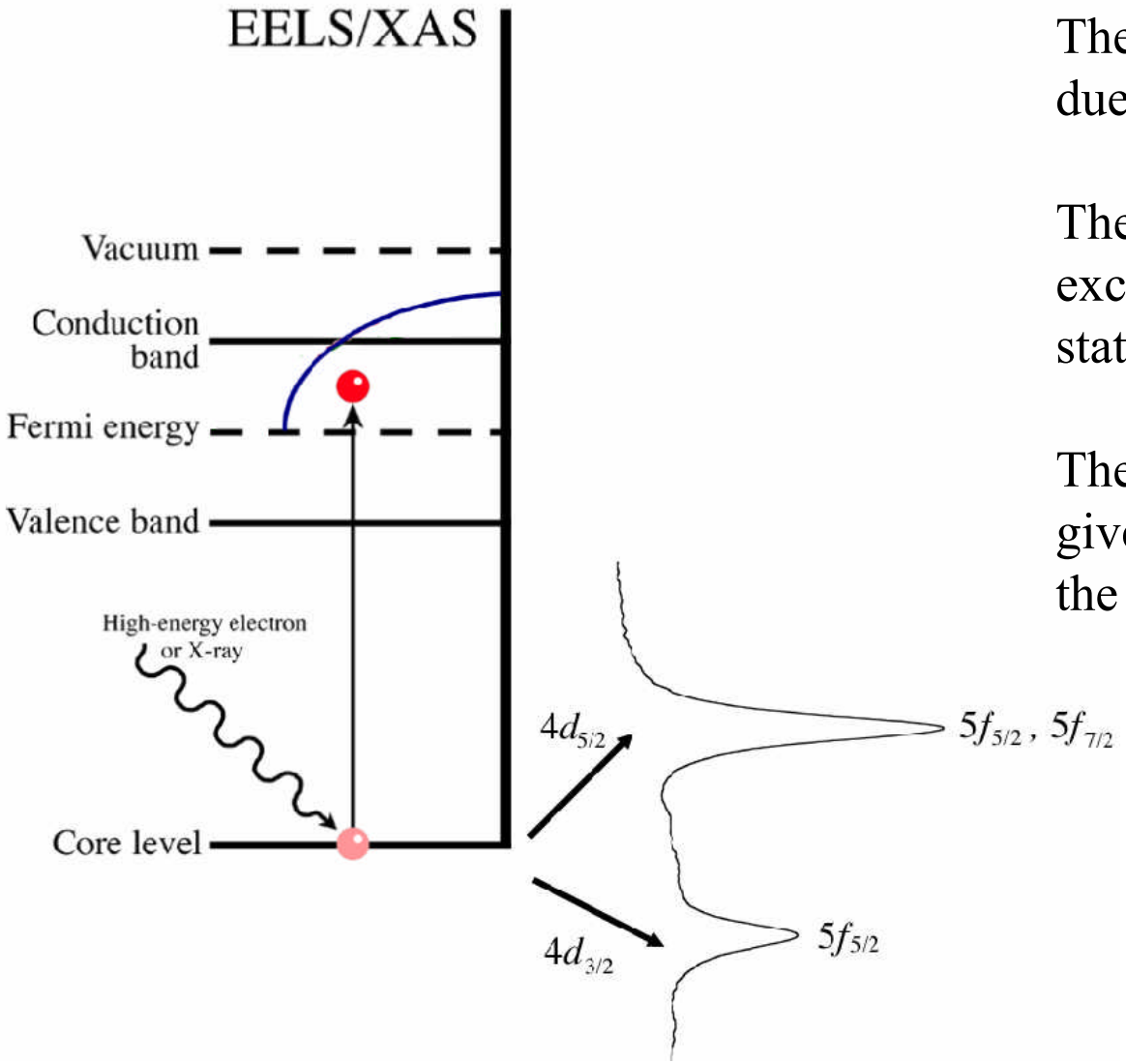


EFTEM


primary electron beam
specimen
angle-limiting aperature (β)
elastically and inelastically scattered electrons
Magnetic Prism
Imaging lenses
energy-selecting slit (Δ)
CCD Camera


specimen
prism
slit
CCD-camera

Branching ratio and dipole selection rules

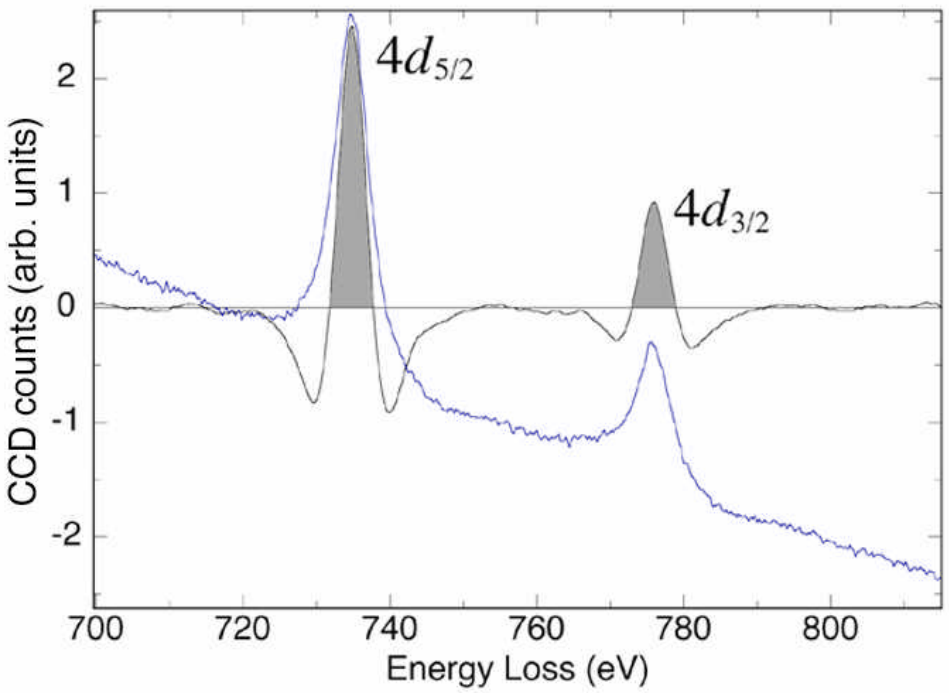


The branching ratio emanates due to dipole selection rules.

The core 4*d* states can only be excited to specific 5*f* final states.

The intensity in each peak gives us information about how the 5*f* states are occupied.

Extracting the branching ratio from EELS spectra



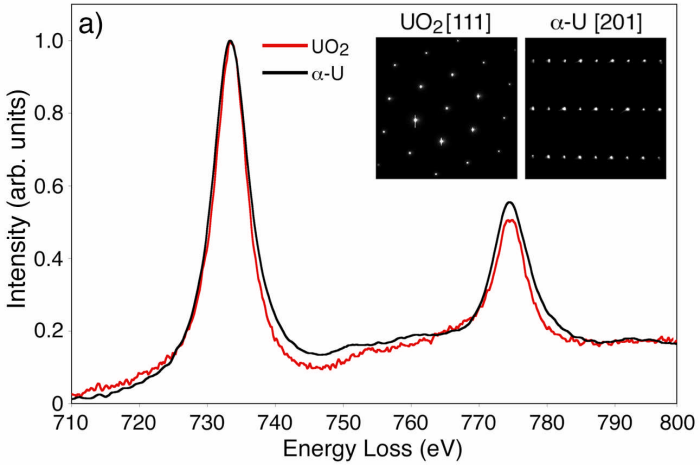
The branching ratio B is defined as:

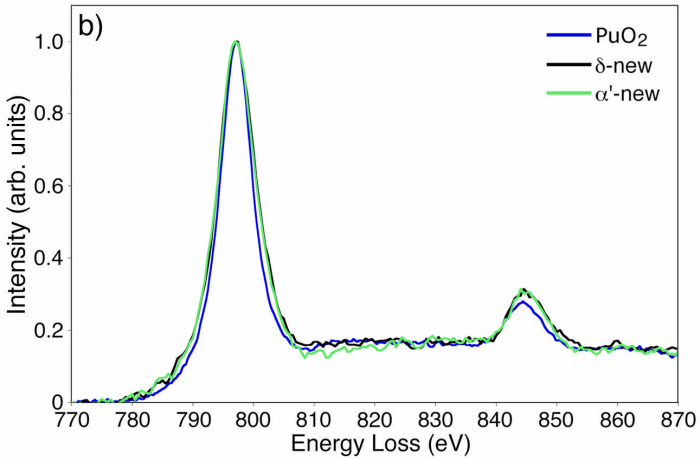
$$B = \frac{A_{5/2}}{[A_{5/2} + A_{3/2}]}$$

where $A_{5/2}$ and $A_{3/2}$ are the areas under the N_5 and N_4 peaks, respectively, in the EELS spectra.

In order to extract the peak areas $A_{5/2}$ and $A_{3/2}$ we take the second derivative (black line) of the raw spectra (blue line) and integrate above the zero, which is the gray areas in the plot above.

This has proven to be a very precise way of measuring the peak areas in our EELS spectra without the need of a background removal procedure.





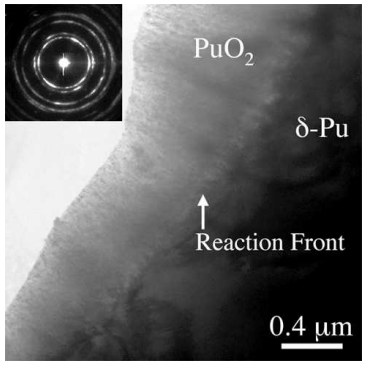
Branching ratio of metal vs. oxides

Left are a number of $N_{4,5}$ EELS spectra:

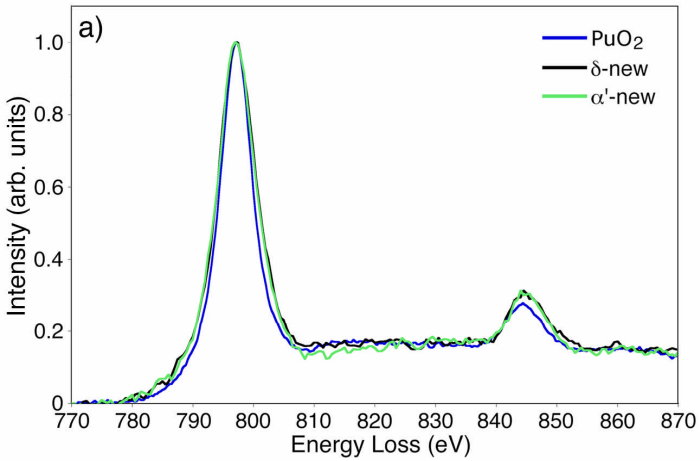
- ↳ a) α-U and UO_2.
- ↳ b) new α'-Pu, new δ-Pu, and PuO_2.

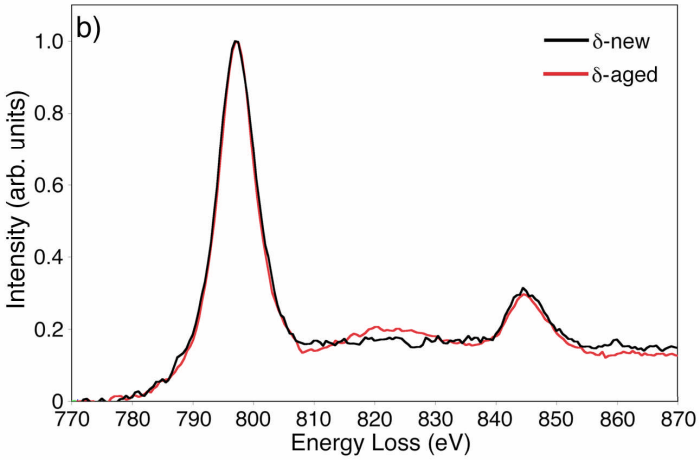
The branching ratio clearly changes between the oxide and metal phases for U and Pu, since the N_4 ($A_{3/2}$) peak changes.

The diffraction patterns in the upper left of (a) show the phases being examined.



PuO_2 was formed in the microscope by allowing a metal sample to oxidize. The polycrystalline diffraction patterns matches the dioxide.





Branching ratio of new vs. old metal

Left are a number of $N_{4,5}$ EELS spectra:

- a) PuO_2, new α'-Pu, and new δ-Pu.
- b) new δ-Pu and aged δ-Pu.

The branching ratio does not visually appear different between the new α'-Pu and the new δ-Pu

The branching ratio shows more difference visually between the new and aged δ-Pu.

Using the branching ratio for spin-orbit analysis: the nuts and bolts

The branching ratios from the spectra yield the spin-orbit interaction per hole.

For the f shell, the expectation value of the angular part of the spin-orbit parameter is $\langle w^{110} \rangle = 2/3 \langle l \cdot s \rangle = n_{7/2} - 4/3\ n_{5/2}$, where $n_{7/2}$ and $n_{5/2}$ are the electron occupation numbers for the angular-momentum levels $j = 7/2$ and $5/2$.

Thus, $\langle w^{110} \rangle$ reveals the proper angular momentum coupling scheme for a given material. For the $d \rightarrow f$ transition, the sum rule gives the spin-orbit interaction per hole as:

$$\frac{\langle w^{110} \rangle}{n_h} - \Delta = -\frac{5}{2}\left(B - \frac{3}{5}\right)$$

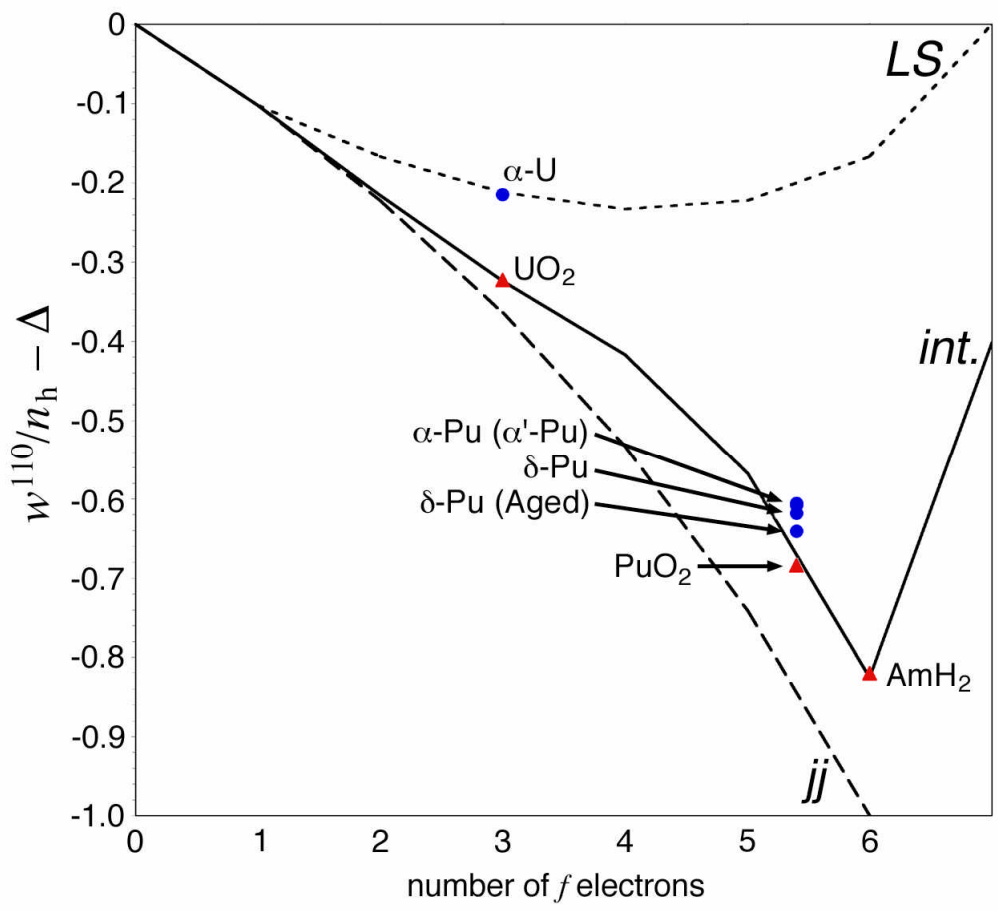
where B is the branching ratio for the experimental spectra, and n_{h} is the number of holes in the f shell, Δ is a correction term that we have shown to almost be zero for the actinides (van der Laan *et al. PRL* **93** 2004).

Branching ratio is changing for oxidation and aging

	Ga content weight %	*f* count	Branching ratio (*B*)	$\frac{\langle w^{110} \rangle}{n_h} - \Delta$
α-U		3	0.686 (002)	–0.215 (005)
UO_2		3	0.729 (001)	–0.3225 (0005)
α-Pu new		5.4	0.843 (010)	–0.6075 (0250)
α'-Pu new	0.6	5.4	0.842 (006)	–0.605 (015)
δ-Pu new	0.6	5.4	0.847 (005)	–0.6174 (0126)
δ-Pu aged	1.0	5.4	0.856 (NA)	–0.64
PuO_2	0.6	5.4	0.874 (014)	–0.685 (035)
AmH_2		6	0.928 (008)	–0.82 (020)

The Ga content in weight %, the perceived *f*-electron count, the experimental branching ratio, *B*, of the $N_{4,5}$ EELS spectra, and the expectation value of the 5*f* spin-orbit interaction per hole, $\langle w^{110} \rangle / n_h$ for each material examined.

Spin-orbit interaction as a function of *f* electrons



Left is a plot of the spin-orbit tensor w^{110} as a function of the number of *f* electrons.

The spin-orbit sum rule does not yield the *f* count, so we assign the 5*f*-electron count via guidance by literature and by the fact that oxides, as localized systems, should be directly on the intermediate coupling curve. Thus, U is assumed as $f = 3$ and Pu as $f = 5.4$.

Now what does this say about oxide bonding and aging?

Our data suggests that U and Pu dioxides are covalently bonded

UO_2 and PuO_2 have a lower $w^{110}/n_h - \Delta$ value than their metal forms due to a increase in the branching ratio.

For a purely ionic transfer of charge: U should be f^2 and Pu f^4 , having given up four electrons.

However, if we plot the oxides with this number of *f* electrons, we find that they are outside the *jj* coupling limit. This is not physically possible, since *jj* coupling corresponds to the end limit where all electrons go into the $j = 5/2$ level, until this level is full.

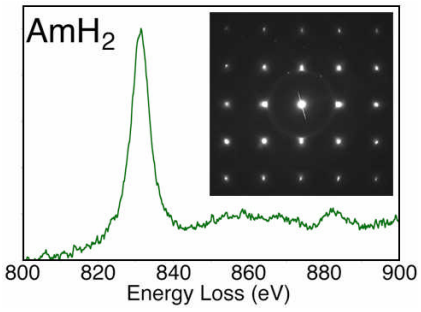
With this in mind, we propose the avant-garde idea that UO_2 and PuO_2 do not have an f^2 or f^4 configuration, respectively. Rather, each element retains a similar *f*-electron count in the dioxide as the metal due to **covalent metal-oxide bonding**.

Additional evidence for covalent bonding in actinide dioxides

➢ Recent experiments (S. D. Conradson *et al. J. Am. Chem. Soc.* **126**, (2004)) and theory (C. J. Burns, *Science* **309**, 1823 (2005)) of solid-state actinide oxides shows significant similarities to molecular systems, meaning that the metal-oxide bonds are covalent in nature.

➢ X-ray absorption experiments with full multiple-scattering (MS) simulations of the O *K*-edge of UO_2 (F. Jollet et al. *J. Phys.: Condens. Matter* **9**, (1997)) and photoemission spectroscopy (J.R. Naegele et al. *Structure and Bonding* **197**, (1985)) indicate covalent bonding between uranium and oxygen.

➢ X-ray and ultraviolet photoelectron spectroscopy of Am thin-films (T. Gouder *et al. Phys. Rev. B* **72**, 2005)) show Am oxide is exhibiting considerable covalent nature.



As one further data set, we measured the branching ratio from EELS and calculated $w^{110}/n_h - \Delta$ for AmH_2 (fcc; a = 5.348Å). If we accept any integer number less than $f = 6$, we find $w^{110}/n_h - \Delta$ would fall beyond the *jj* limit, which is not physically possible.

Spin-orbit analysis of Pu aging

The trend of the $w^{110}/n_h - \Delta$ values for Pu metals and alloys is just as one would expect: α-Pu and α′-Pu have the highest value, Ga-stabilized δ-Pu is slightly lower, and finally, aged, Ga-stabilized δ-Pu has the lowest value.

- ↳ α-phase is much denser crystallographically and it is broadly accepted to have the strongest *f*-electron hybridization. Thus, it should be the closest to the *LS* limit.
- ↳ δ-Pu, which has a considerably expanded lattice compared to α and correspondingly more localized *f* states, falls closer to the *jj* limit.
- ↳ Finally, aged, Ga-stabilized δ-Pu falls the closest to the *jj* limit of all the Pu metals - aged lattice is expanded due to accumulated damage from self-irradiation, further localizing the *f* states.

Right at detectibility limit of technique: The standard deviations just overlap.

The trend in data was reproducible over numerous areas of each α+δ sample, giving further confidence in the data, yet we need more experiments to be sure.

Thus, EELS in a TEM and the spin-orbit sum rule may represent the an experimental technique sensitive enough to detect changes in the *bulk* electronic structure of actinide metals caused by self-irradiation damage.

Summary

- The spin-orbit sum rule can detect changes in the *f* states between U and Pu metal and UO_2 and PuO_2.

- Our data suggest bonding in UO_2 and PuO_2 is covalent in nature.

- The idea of covalent metal-oxide bonds has recently come to the forefront of actinide chemistry (C. J. Burns, *Science* **309**, 1823 (2005)), and our data supports the assertion.

- The spin-orbit sum rule shows changes between new and aged Pu.

- The data trends in the correct fashion; α- and α′-Pu, δ-Pu, aged δ-Pu, where α-Pu is closest to the *LS* limit and aged δ-Pu is closest to the *jj* limit.

- EELS and the spin-orbit sum rule could be used a probe for tracking changes in the bulk electronic structure due to self-irradiation damage with time.